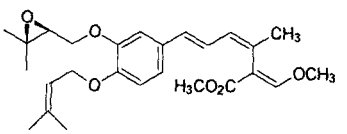
Table 2. Spectrum of fungicidal action of 9-methoxystrobilurin A and K (– : no inhibition observed; values with i: incomplete inhibition).

Test organism	Diameter of inhibition zone [mm] 9-Methoxystrobilurin A (3) µg per disc [a]		9-Methoxystrobilurin K (4) µg per disc [a]	
	0.1	1	0.1	1
Absidia glauca (+)	–	15 i	–	10
Absidia glauca (–)	17 i	26 i	14	20
Alternaria porri	35 i	52 i	18 i	28 i
Aspergillus ochraceus	18 i	34 i	15 i	24 i
Epicoccum purpurascens	22 i	24 i	10 i	15 i
Fusarium oxysporum	24 i	35 i	–	12 i
Fusarium fujikuroi	32 i	40 i	12 i	15 i
Mucor miehei	23	37	14	20
Paecilomyces variotii	21 i	36 i	15 i	22 i
Penicillium islandicum	11 i	17 i	10 i	18 i
Penicillium notatum	26 i	37 i	15 i	21 i
Rhodotorula glutinis	15 i	25 i	10 i	17 i
Ustilago nuda	20 i	28 i	14 i	20 i
Zygorrhynchus moelleri	13 i	20 i	–	13 i

[a] Diameter 6 mm.

respiratory inhibition due to 9-methoxystrobilurin resembles that of strobilurin A and oudemansin A, which shows that substitution of a methoxy group at C-9 on strobilurin A does not influence its effect on respiration. The 9-methoxy derivatives, like strobilurin E,[11] have cytostatic properties. HeLa S3 cells show pronounced inhibition of growth and changes in morphology in the presence of 2 $\mu g\,mL^{-1}$ (6.94 µM) **3** and 4 $ng\,mL^{-1}$ (8.47 nM) **4**. Whilst the cytostatic activity of **3** is similar to that of strobilurin A in this test system, the extraordinarily large effect of **4** on the HeLa S3 cells is comparable with that of strobilurin D (**6**).



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Keywords: strobilurins · oudemansins · fungicides · antibiotics

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[7] 4-Hydroxystrobilurin D, which is related and has an (*S*)-2-(3-methyl-2,3-epoxybutyloxy) substituent [8], exhibits an optical rotation of $[\alpha]_D^{22} = +22$ ($c = 0.3$, $CHCl_3$). Because of the different chromophore, the negative rotation of **4** ($[\alpha]_D^{22} = -8.8$ ($c = 0.8$, $CHCl_3$)) does not allow any reliable conclusions about the absolute configuration to be drawn. The CD curves also show no obvious mirror-image trend.

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2,4-Di-*tert*-butyl-1λ^3,3λ^3-diphosphinines: Targeted Synthesis at Iron(0) Centers and Oxidative Release**

Dieter Böhm, Falk Knoch, Susanne Kummer, Uwe Schmidt, and Ulrich Zenneck*

Dedicated to Professor Peter Paetzold on the occasion of his 60th birthday

Trivalent phosphorus atoms and CR fragments are isoelectronic building blocks that can occupy equivalent positions in many organophosphorus compounds, for example in heteroarenes. The simplest member of this group, λ^3-phosphinine (phosphabenzene)[1] is known, as well as many of its substitution products.[2] Phosphinines can act as σ-donor ligands, utilizing the lone pair on phosphorus, and also as cyclic η^6 ligands.[2] Of the three possible diphosphinine isomers, only 2,3,5,6-tetrakis(trifluoromethyl)-1λ^3,4λ^3-diphosphinine has so far been prepared in solution and spectroscopically characterized.[3] There is also very little known about phosphorus-rich benzene analogues. A cyclotrimerization product of *tert*-butylphosphaethyne **1**[4] has been characterized as a π-bound triphosphadewarbenzene.[5] A second trimerization product of **1** was postulated to be a coordinated 1,3,5-triphosphinine;[6] this, however, has not yet been definitively proven.[7] We report here an efficient synthesis of 1λ^3,3λ^3-diphosphinines in the coordination sphere of iron(0) by [2 + 2 + 2] cycloaddition of two phosphaalkynes and a terminal alkyne. The release of these 1λ^3,3λ^3-diphosphinines under oxidative conditions is also discussed.

The reaction of bis(η^2-ethylene)(η^6-toluene)iron **2**[8] with *tert*-butylphosphaethyne **1** at moderate temperatures (maximum room temperature) yields, apart from the cyclodimerization of **1** to a coordinated 1,3-diphosphete in (η^4-2,4-di-*tert*-butyl-1,3-diphosphete)(η^6-toluene)iron **3**, a surprising formation of five-membered rings. This leads to a pentaphosphaferrocene, penta-*tert*-butyl-(1,2,4-triphospholyl)(1,3-diphospholyl)iron (**4**).[9] During this reaction, at least one phosphaalkyne molecule must undergo cleavage of the triple bond,[9] and the trimerization of the phosphaalkyne **1** is avoided in this case. Normally, this reaction predominates during the interaction of **2** with alkynes.[10]

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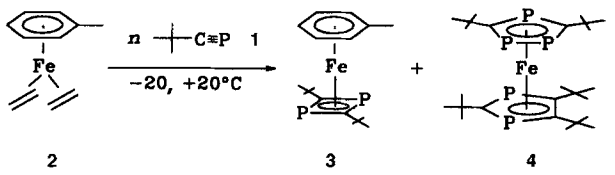
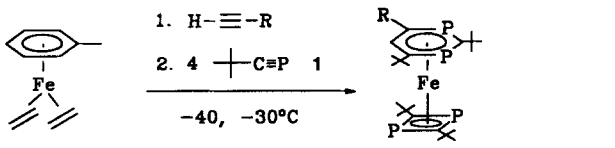


The reaction of **2** with acetylene at $-40\,^{\circ}C$ or with terminal alkynes at $-30\,^{\circ}C$, followed by a reaction with **1**, leads to a suppression of the five-membered ring formation, and apart from small quantities of **3** and **4**, the stable sandwich complexes **5a–e**, which contain 2,4-di-*tert*-butyl-1λ^3,3λ^3-diphosphinines



5a, R = H (55%)
5b, R = $CH_2OC(O)CH_3$ (35%)
5c, R = n-C_4H_9 (40%)
5d, R = CH_2OH (35%)
5e, R = CH_2OCH_3 (35%)

and 2,4-di-*tert*-butyl-1λ^3,3λ^3-diphosphete as ligands, are obtained. If **1** is added to **2** before the addition of the alkyne, the same products result; however, the yields of **5a–e** are significantly lower. The [2 + 2 + 2] cycloaddition of two molecules of **1** and one acetylene molecule (or a different alkyne) is regiospecific in two ways: only 1,3-diphosphinines are formed, but no 1,4-derivatives, and the substituent introduced with the alkyne always ends up in the position neighboring the P atom. The reaction fails with 3,3-dimethylbutyne and internal alkynes; functional groups on 1-alkynes, such as hydroxyl, ethers, or esters, are tolerated.

According to the spectroscopic data (Table 1) and the single-crystal X-ray structure analyses of **5a** (Fig. 1) and **5b**,[11] the

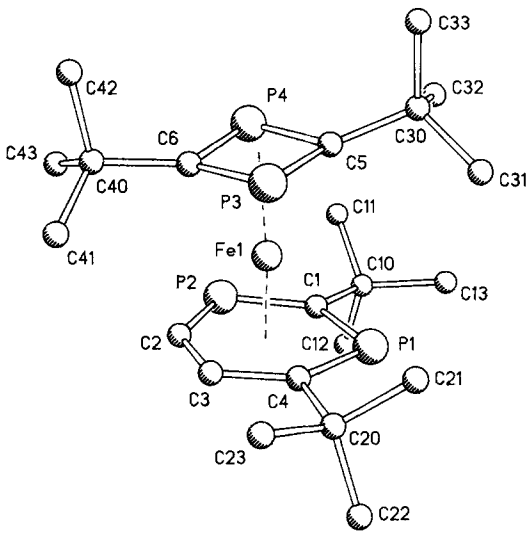


Fig 1. Structure of **5a** in the crystal. Selected bond lengths [Å] and angles [°]: Fe–P1 2.388(5), Fe–P2 2.387(6), Fe–P3 2.288(5), Fe–P4 2.306(5), Fe–C1 2.218(14), Fe–C2 2.163(17), Fe–C3 2.223(16), Fe–C4 2.173(15), Fe–C5 2.166(16), Fe–C6 2.110(14), P1–C1 1.738(16), P1–C4 1.763(16), P2–C1 1.760(15), P2–C2 1.769(17), P3–C5 1.769(17), P3–C6 1.770(15), P4–C5 1.782(17), P4–C6 1.774(17), C1–C10 1.584(23), C2–C3 1.436(23), C3–C4 1.510(22), C4–C20 1.519(23), C5–C30 1.524(24), C6–C40 1.542(20); C1-P1-C4 105.7(7), C1-P2-C2 103.0(8), C5-P3-C6 80.9(8), C5-P4-C6 80.5(7), P1-C1-P2 131.0(10), P2-C2-C3 131.8(13), C2-C3-C4 120.8(14), P1-C4-C3 127.5(12), P3-C5-P4 99.1(9), P3-C6-P4 99.3(7).

η^6-ligated 1,3-diphosphinines are essentially planar six-membered heteroarenes. The deviations of the ring atoms from the least-squares planes of the 1,3-diphosphinines range from + 3.1 to −1.9 pm for **5a** and +1.8 to −1.6 pm for **5b**. The data agree well with those obtained for η^6-coordinated phosphinines.[1,2] The distance between two of the sp^2 ring carbon atoms of **5a** (C3 and C4) is surprisingly large (151 pm), the same length as the single bond between C4 and C20. In contrast, the equivalent C3–C4 distance in **5b** (142 pm) is in the expected range. The reasons behind the large C–C distance in the ring of **5a** are not yet clear.

Table 1. Selected spectroscopic data for **5a,b** and **6a,b** [a].

5a: All NMR spectra represent the slow exchange limit. ^{1}H NMR (269.60 MHz, C_7D_8, 243 K, TMS): δ = 1.55 (s, 18H, Me at C10 and C20), 0.86 (s, 9H, Me at C30), 1.07 (s, 9H, Me at C40), 5.53 (ddd, 1H, H at C2, J(H,H) = 9.4, J(H,P) = 35.5, J(H,P) = 0.7 Hz), 6.10 (ddd, 1H, H at C3, J(H,P) = 5.5, J(H,P) = 8.5 Hz); ^{31}P{^{1}H} NMR (109.37 MHz, C_7H_8, 295 K, 85% H_3PO_4 (ext.)): δ = 10.8 (ddd, 1P, P2, J(P,P) = 12.4, J(P,P) = 8.7, J(P,P) = 5.4 Hz), 27.8 (d, 1P, P1, J(P,P) = 12.4 Hz), 30.7 (br, 1P, P4), 40.0 (br, 1P, P3); ^{13}C{^{1}H} NMR (67.7 MHz, C_7D_8, 298 K, TMS): δ = 34.8 (t, Me a C10, J(C,P) = 19.7 Hz), 32.8 (d, Me at C20, J(C,P) = 16.9 Hz), 30.8 (s, Me at C30), 33.3 (s, Me at C40), 40.7 (t, C10, J(C,P) = 36.7 Hz), 39.0 (d, C20, J(C,P) = 38.4 Hz), 35.2 (t, C30, J(C,P) = 11.3 Hz), 35.7 (t, C40, J(C,P) = 11.3 Hz), 133.5(dd, C1, J(C,P) = 73.3, J(C,P) = 84.6 Hz), 122.8 (dd, C4, J(C,P) = 71.1, J(C,P) = 4.5 Hz), 101.5 (t, C5, J(C,P) = 57.5Hz), 107.9 (t, C6, J(C,P) = 57.5 Hz), 90.7 (dd, C2, J(C,P) = 62.1, J(C,P) = 3.1 Hz), 91.3 (t, C3, J(C,P) = 8.5 Hz); EI-MS (70 eV): m/z (%): 482 (73) [M^+], 28 (100).

5b: ^{1}H NMR (60 MHz, $CDCl_3$, 295 K, TMS): δ = 1.00 (s, 18H, 2 tBu), 1.55 (s, 9H, tBu), 1.65 (s, 9H, tBu), 2.10 (s, CH_3), 5.15 (d, 2H, CH_2, J(H,P) = 14.0 Hz), 7.00 (t, 1H, H at C3, J(H,P) = 6.0 Hz); ^{31}P{^{1}H} NMR (109.37 MHz, $CDCl_3$, 295 K, 85% H_3PO_4 (ext.)): δ = 14.1 (d, 1P, P2, J(P,P) = 18.22 Hz), 16.1 (d, 1P, P1), 35.0 (s, 2P, P3 and P4); ^{13}C{^{1}H} NMR (67.7 MHz, $CDCl_3$, 295 K, TMS): δ = 22.0 (s, C9), 31.5 (d, Me at C20, J(C,P) = 11.3 Hz), 33.0 (s, Me at C30 and C40), 35.5 (t, Me at C10, J(C,P) = 19.9 Hz), 36.5 (d, C30 and C40, J(C,P) = 11.3 Hz), 39.5 (d, C20, J(C,P) = 19.8 Hz), 42.0 (t, C10, J(C,P) = 22.6 Hz), 73.0 (d, C7, J(C,P) = 19.6 Hz), 97.0 (s, C8), 102.0 (dd, C4, J(C,P) = 63.9, J(C,P) = 7.5 Hz), 111.0 (t, C3, J(C,P) = 25.3 Hz), 127.0 (dd, C2, J(C,P) = 73.9, J(C,P) = 3.1 Hz), 137.0 (dd, C1, J(C,P) = 82.1, J(C,P) = 73.9 Hz); EI-MS (70 eV): m/z (%): 554 (98) [M^+], 354 (100) [M^+−(tBuCP)$_2$].

6a: ^{1}H NMR (269.60 MHz, $CDCl_3$, 295 K, TMS): δ = 1.52 (d, 9H, Me at C20, J(H,P) = 1.5 Hz), 1.67 (t, 9H, Me at C10, J(H,P) = 1.5 Hz), 8.06 (ddd, 1H, H at C3, J(H,P) = 11.1, J (H,P) = 6.8, J(H,H) = 11.1 Hz), 8.78 (ddd, 1H, H at C2, J(H,P) = 41.8, J(H,H) = 4.3, J(H,H) 11.1 Hz); ^{31}P{^{1}H} NMR (109.37 MHz, $CDCl_3$, 295 K, 85% H_3PO_4 (ext.)): δ = 220.2 (d, P2, J(P,P) = 24.7 Hz), 237.9 (d, P1, J(P,P) = 24.7 Hz); ^{13}C{^{1}H} NMR (67.7 MHz, $CDCl_3$, 295 K, TMS): δ = 33.0 (d, 3C, C21, C22, and C23, J(C,P) = 12.2 Hz), 35.4 (t, C11, C12, and C13, J(C,P) = 13.0 Hz), 40.0 (d, C20, J(C,P) = 24.4 Hz), 43.1 (d, C10, J(C,P) = 20.5 Hz), 129.9 (dd, C3, J(C,P) = 13.5, J(C,P) = 9.9 Hz), 150.7 (dd, C2, J(C,P) = 51.8, J(C,P) = 15.2 Hz), 181.2 (dd, C2, J(C,P) = 63.9, J(C,P) = 18.3 Hz), 217.1 (dd, C1, J(C,P) = 76.9, J(C,P) = 70.8 Hz).

6b: ^{1}H NMR (60 MHz, $CDCl_3$, 295 K, TMS): δ = 1.89 (t, 9H, Me at C20, J(H,P) = 6.0 Hz), 1.73 (t, 9H, Me at C10, J(H,P) = 8.0 Hz), 2.08 (s, 3H, Me at C9), 5.47 (dd, 2H, at C7, J(H,P) = 14.0, J(H,P) = 4.0 Hz), 8.03 (t, 1H at C3, J(H,P) = 8.0 Hz); ^{31}P{^{1}H} NMR (109.37 MHz, $CDCl_3$, 295 K, 85% H_3PO_4 (ext.)): δ = 222.5 (d, P2, J(P,P) = 21.0 Hz), 235.5 (d, P2, J(P,P) = 21.0 Hz); ^{13}C{^{1}H} NMR (67.7 MHz, $CDCl_3$, 295 K, TMS): δ = 20.0 (s, C9), 31.0 (d, C21, C22, and C23, J(C,P) = 12.2 Hz), 34.0 (t, C11, C12, and C13, J(C,P) = 12.9 Hz), 39.0 (d, C20, J(C,P) = 22.9 Hz), 42.0 (t, C10, J(C,P) = 21.3 Hz), 69.0 (d, C7, J(C,P) = 47.3 Hz), 131.0 (t, C3, J(C,P) = 10.7 Hz), 160.0 (dd, C4, J(C,P) = 50.3, J(C,P) = 15.2 Hz), 169.0 (s, C8), 181.0 (dd, C2, J(C,P) = 64.0, J(C,P) = 15.2 Hz), 216.0 (dd, C1, J(C,P) = 76.2, J(C,P) = 70.1 Hz).

[a] Atom numbering as in Fig. 1.

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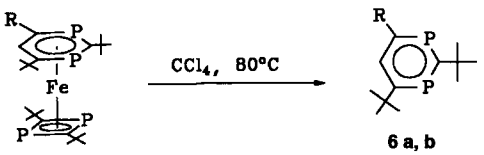
The NMR spectra (^1H, ^{13}C, ^{31}P) of **5a** are temperature-dependent owing to the hindered rotation of both cyclic ligands, which carry two *tert*-butyl groups each. The rotation barrier $\Delta G^{\ddagger}_{rot}$ is 55 kJ mol^{-1}. For **5b–e**, the NMR spectra represent the rapid exchange limit. Line broadening is observed for some signals only below $-80\,^{\circ}C$, hence $\Delta G^{\ddagger}_{rot}$ is smaller than 30 kJ mol^{-1}. This can be explained by the interaction between the R substituents and one of the *tert*-butyl groups of the diphosphete.

The compounds **3** and **5a–e** are structurally analogous complexes in which the toluene and the diphosphinine ligands, which, to our knowledge, are described here for the first time, occupy equivalent positions. Consequently, the spectroscopic properties of these species are quite similar.[9] There are, however, big differences in the redox behavior: while **3** can be reversibly oxidized and, at low temperatures, reduced electrochemically, the anions and cations of **5a** are so short-lived that on the time scale of cyclic voltammetry, they decompose completely even at low temperatures.[12] Only in situ EPR spectroscopy on the redox products yielded indications of the existence of the ions 5^+ and 5^-. A similar difference has been observed for ferrocene and the pentaphosphaferrocene derivatives **4**[13] as well as (pentamethylcyclopentadienyl)(pentaphospholyl)iron.[14] The latter two species do not yield stable cations, while the ferrocenium ion can be isolated in the form of salts.

We assume the mechanism of formation to proceed by an initial replacement of one or both ethylene ligands in **2** by the alkyne. Subsequently, four molecules of **1** are added in a stepwise fashion and the toluene ligand is lost. The two heterocycles are probably formed via ferraphospha- and ferradiphosphacyclopentadiene intermediates, respectively. Stable cycloaddition products of this type have been demonstrated for a $1\lambda^3$-phospha-3-zirconacyclopenta-1,4-diene[15] and a $1\lambda^3,4\lambda^3$-diphospha-2-rhodacyclopenta-3,5-diene.[16]

The oxidative decomplexation of the 1,3-diphosphinines succeeds with $FeCl_3$ or halogenated hydrocarbons at elevated temperatures. The most useful reaction for preparative purposes is the treatment of **5a** and **5b** with CCl_4, which releases **6a** and **6b**, respectively.



a, R = H

b, R = $CH_2OC(O)CH_3$

According to their NMR spectra (^1H, ^{13}C, ^{31}P), the stable free 1,3-diphosphinines **6a,b** can be classified as π^6 heteroarenes (Table 1). The relationship to phosphinines is clearly apparent and the spectroscopic findings are incompatible with alternative structures, such as Dewar-diphosphinine, diphosphaprismane, or diphosphabenzvalene. This has also been confirmed by comparing the ^1H, ^{13}C, and ^{31}P NMR spectra of **6a** and **6b** with those of the isomers of phosphinine.[17] The successful release of **6a** and **6b** completes their synthesis from simple precursors at the transition metal center. The novel rings are now available for further work. Studies concerning their organoelement and coordination chemistry are currently underway. Metal complexes of **6a** and **6b** with labile co-ligands are of particular interest as potential catalysts, for instance for the synthesis of pyridines.[18]

Experimental Procedure

5a–e: A solution of **2** (0.52 g, 2.5 mmol) was prepared in toluene (70 mL) at $-40\,^{\circ}C$, under an inert gas atmosphere. The mixture was either saturated with acetylene or treated at $-30\,^{\circ}C$ with 2-propynyl acetate (0.74 g, 7.5 mmol). At $-30\,^{\circ}C$, **1** (1.0 g, 10 mmol) in toluene (20 mL) was added, and the solution was allowed to warm to room temperature over a period of 3 h. The solvent was subsequently removed under vacuum (0.01 mbar). The black residue was taken up in petroleum ether and filtered through a small amount of Al_2O_3 (5% H_2O), which was washed with petroleum ether. The solution was reduced in volume and subjected to chromatography on SiO_2 (5% H_2O).

The reaction with acetylene and the use of petroleum ether as eluant yielded **5a** (662 mg, 1.37 mmol, 55%) as dark red, analytically pure crystals. A second fraction afforded the isolation of **3** in 12% yield.

The reaction with 2-propynyl acetate combined with the use of petroleum acetate/toluene (5:1) as eluant led to the isolation of **5b**. After recrystallization, **5b** was obtained in an analytically pure form (387 mg, 0.7 mmol, 35%).

Compounds **5c–e** can be prepared in an analogous manner (see Scheme 2 for yields).

6b: **5b** (1.06 g, 1.9 mmol) was dissolved in CCl_4 (20 mL), and the solution was heated to reflux. After 1 h the solution was filtered through Al_2O_3 and the solvent was distilled off. Subsequent vacuum distillation (2 Pa) yielded **6b** as the first fraction (130 °C) in the form of a yellow oil (143 mg, 0.48 mmol, 25%). Further fractions collected at higher temperatures contained only small portions of **6b**. The diphosphinine **6a** was obtained from **5a** in an analogous manner.

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[12] By cyclic voltammetry, only irreversible electron transfer reactions were found for **5a** and **5b**: for instance, for **5a** at a glassy carbon electrode in 1,2-dimethoxyethane, using $(n\mathrm{Bu})_4\mathrm{NPF}_6$ as supporting electrolyte, at $E_{p(ox)} = 0.86$ V and $E_{p(red)} = -1.84$ V (referenced to the saturated calomel electrode); D. Böhm, H. Meth, U. Zenneck, unpublished results.
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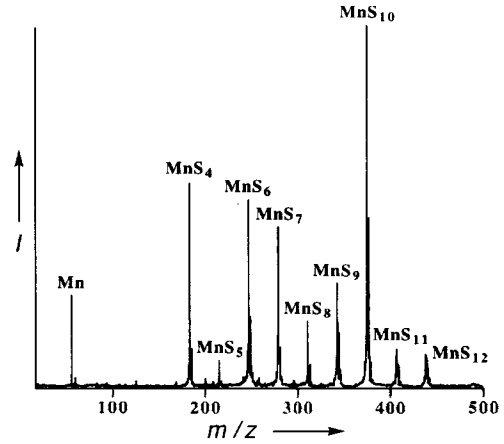

Fig. 1. Mass spectrum of the (positive) products of the reaction between Mn^+ and S_8 at $2-3\times10^{-8}$ mbar. The spectrum was recorded after a reaction period of 10 s, that is, after all of the Mn^+ has reacted.

Formation and Structures of New Metallo- and Metallapolysulfanes, $[MS_y]^+$ ($y = 2-16$)**

Ian Dance,* Keith Fisher, and Gary Willett

Amongst the growing knowledge and understanding of the reactions of ligands with bare metal ions in the gas phase[1] there is scanty information about reactions with sulfur,[2, 3] although metallapolysulfane ions are known to be formed in reactions with ethylenesulfide.[3, 4] While investigating the formation and structures of clusters $[M_xS_y]^-$ generated subsequent to laser ablation of metal sulfides,[5] we observed the formation of $[MS_y]^+$ ions, presumably from elemental sulfur released during laser ablation. Subsequently we discovered that there is a general reaction of $M^+_{(g)}$ with $S_{8(g)}$ to form series of metallapolysulfane complexes $[MS_y]^+$ for most elements of the periodic table. We report here on the ions $[MS_y]^+$ ($y = 2-16$) for first row transition metals, and present some results of density functional computations of the structures of major species.

The metal ions $M^+_{(g)}$ were generated by laser ablation of the metal (Ti, V, Cr, Co, Ni, Cu, Zn), metal oxide (Sc), or the metal sulfide (Mn, Fe) in the ion trap of a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer, while a capillary containing sulfur provided a background sulfur pressure of $2-3\times10^{-8}$ mbar. The trapped metal ions M^+ were allowed to undergo collisional cooling for periods of 0.1–2 s, then all other ions were ejected from the cell, and the reactions of the thermalized M^+ ions with the excess S_8 [6] were monitored for periods of up to 100 s. A representative spectrum for Mn is shown in Figure 1.

The major and minor products for all of the first row transition metals are listed in Table 1, with indications of the reaction time scales. The conversion of the M^+ ions appears to be pseudo first order for all metals. Only in the case of Zn^+ ions is the S_8^+ ion a major product. This is probably formed by charge transfer between the S_8 molecules and one of the zinc polysulfanes, not by rapid resonant charge transfer with the Zn^+ ions.[7]

Table 1. Positive ion products of the reactions of thermalized metal ions $M^+_{(g)}$ with excess sulfur vapor at $2-3\times10^{-8}$ mbar.

Metall	Major products (t/s)	Minor products
Sc^+	$[ScS_4]^+$ (1–5), $[ScS_{10}]^+$ (5–50), $[ScS_{12}]^+$ (>50)	$[ScS_2]^+$, $[ScS_6]^+$, $[ScS_8]^+$, $[ScS_9]^+$, $[ScS_{11}]^+$, $[ScS_{13}]^+$, $[ScS_{14}]^+$ [a]
Ti^+	$[TiS_4]^+$ (<8), $[TiS_8]^+$ (>8)	$[TiS_6]^+$, $[TiOS_6]^+$ [b], $[TiS_{10}]^+$, $[TiS_{12}]^+$ [a]
V^+	$[VS_4]^+$ (<8), $[VS_8]^+$ (>8)	$[VS_2]^+$, $[VS_5]^+$, $[VS_6]^+$, $[VS_7]^+$, $[VS_9]^+$, $[VS_{10}]^+$
Cr^+	$[CrS_4]^+$ (<10), $[CrS_8]^+$ (>10)	$[CrS_6]^+$, $[CrS_{10}]^+$
Mn^+	$[MnS_4]^+$ (<8), $[MnS_{10}]^+$ (>8)	$[MnS_5]^+$ [a], $[MnS_6]^+$, $[MnS_7]^+$, $[MnS_8]^+$, $[MnS_9]^+$, $[MnS_{11}]^+$, $[MnS_{12}]^+$
Fe^+	$[FeS_4]^+$ (<5), $[FeS_{10}]^+$ (>5)	$[FeS_6]^+$, $[FeS_7]^+$, $[FeS_8]^+$
Co^+	$[CoS_4]^+$ (<30), $[CoS_6]^+$ (30–50), $[CoS_{10}]^+$ (>50)	$[CoS_5]^+$, $[CoS_7]^+$, $[CoS_8]^+$
Ni^+	$[NiS_4]^+$ (<15), $[NiS_{10}]^+$ (>15)	$[NiS_5]^+$, $[NiS_6]^+$, $[NiS_8]^+$
Cu^+	$[CuS_4]^+$ (<20), $[CuS_{12}]^+$ (>20)	$[CuS_4(H_2O)]^+$ [b], $[CuS_8]^+$, $[CuS_{10}]^+$, $[CuS_{13}]^+$, $[CuS_{16}]^+$
Zn^+	$[S_8]^+$	$[ZnS_4]^+$, $[ZnS_4(H_2O)]^+$ [b], $[ZnS_{10}]^+$, $[ZnS_{12}]^+$

[a] Formed in traces. [b] Formed from adventitious water.

The reactivity patterns for M^+ plus S_8 can be summarized as: 1. The relative rates of reaction of M^+ with S_8 are $(Fe \approx Sc) > (Ti \approx V \approx Cr \approx Mn) > (Co \approx Ni) > (Cu \approx Zn)$. These follow atomic number, except for the enhanced reactivity of Fe^+. 2. For all metals except Zn, $[MS_4]^+$ is the first major product. 3. At longer times the major products are $[MS_6]^+$ for M = Co; $[MS_8]^+$ for M = Ti, V, and Cr; $[MS_{10}]^+$ for M = Sc, Mn, Fe, and Ni; and $[MS_{12}]^+$ for M = Sc and Cu. 4. The highest mass ions are $[MS_{10}]^+$ for M = V, Cr, Fe, Co, and Ni; $[MS_{12}]^+$ for M = Ti, Mn, and Zn; $[MS_{14}]^+$ for M = Sc; and $[MS_{16}]^+$ for M = Cu. 5. $[MS_y]^+$ with y odd are not abundant, except for $[VS_7]^+$ and $[MnS_7]^+$.

What are the structures and structural principles for these new complexes? In order to answer this question we used established ab initio density functional theory[8] to explore the structure-energy surfaces of the complexes by optimization of a variety of postulated structures. Jones et al., for example, used local density functional methods coupled with molecular dynamics to map the energy surfaces for sulfur molecules.[9] Here we outline key results for the ions $[MS_4]^+$, $[MS_8]^+$, and $[MS_{12}]^+$: details of all calculated geometrical and electronic structures will be presented separately.

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